

## Magpie Polymers – selective metal capture

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**Abstract** Dissolved transition metals are commonly found in water, such as mine water. Magpie Polymers is a spin-off from the prestigious French institute Ecole Polytechnique, which uses a new patented technology to selectively remove metals from water, generating purified water and valuable metal(s). This effectively transforms the burden of water pollution into an opportunity for metal recovery. We have studied the capturing capabilities of two different types of Magpie Polymers with various metals; this paper is focused on the removal of copper using one of the Magpie polymers.

**Key Words** active treatment, polymers, metals

### Introduction

Selectivity is a major concern when removing transition metals from water in a manner that is both efficient and economically viable. Selective methods do not only allow clean-up of the water, but also the re-use or sale of the extracted metals. Therefore, when designing a new resin for the capture and recycling of metals from water, specific and selective interactions with the metals should be targeted. Coordination chemistry is based on very specific metal-ligand interactions. In this field of chemistry, subtle changes to the ligands' electron donating or accepting properties are made to tune the stability and reactivity of the formed complexes. Typically, such complexes find applications in homogeneous catalysis. Ligands commonly used are amines, thiols or acids, similar to the functionalities found on many of the commercially available ion-exchange resins. In addition, many stable and useful coordination complexes contain phosphines or phosphine oxides. Surprisingly, these functional groups are not commonly found on metal-capturing resins.

We therefore designed a family of polymers containing stable alkylphosphines and phosphine oxides, as shown in figure 1. These materials, referred to as Magpie-101 and Magpie-102 respectively, can be readily formed in kilogram scale in our laboratory using cheap, bulk chemicals only. They provide a unique functionality for the capture and recycling of transition metals. In order to characterize the polymers, a series of tests were performed with Magpie-101 and Magpie-102 and a variety of metals including cadmium, chromium, nickel, lead, palladium and uranium, at different metal concentrations and pH. These results show that the metals are readily captured by the polymers, and can be eluted using strong acid. In the current paper, we discuss the results for copper, revealing the saturation level, kinetics of capture as well as the transparency of the polymers towards calcium.

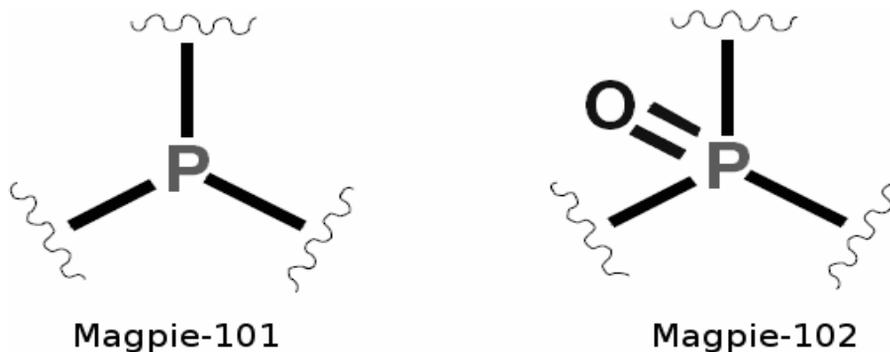


Figure 1 showing the functional group of the Magpie-101 and Magpie-102 resins, respectively

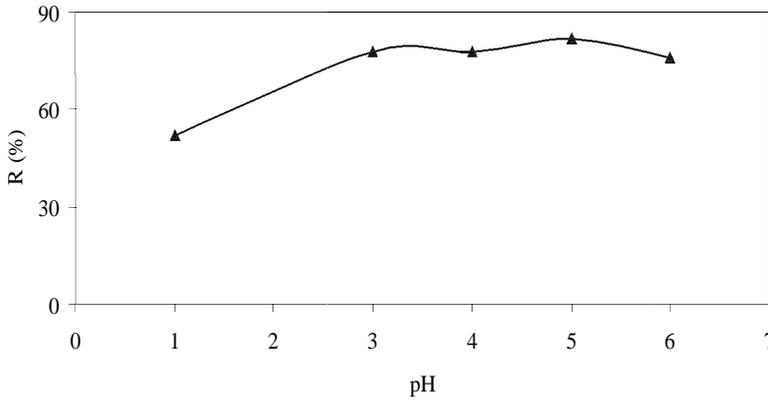


Figure 2 showing the effect of pH on the sorption of Cu(II) by Magpie-101

**Methods**

**Polymer synthesis**

Polymer Magpie-101 was prepared using previously published methods in batches of 250 g with yields between 70 and 80 % (Van Zutphen 2009). The integrity of the polymer was verified using IR spectroscopy. Prior to the tests, the polymer was washed with deionized water. All experiments were carried out at room temperature.

**Optimization of pH**

In general, the complexation of metal ions to ligands or capturing resins will depend on pH levels (Verbych 2006). Although Magpie Polymers cannot be protonated, even at low pH, the solubility of metal ions are a function of pH. We therefore investigated the ability of Magpie-101 to capture Cu(II) ions at a pH between 1.0 and 6.0 ( $c_0 \approx 100 \text{ mg L}^{-1}$ ,  $V = 20 \text{ cm}^3$ , 30 mg of polymer). The results show that retention increases with pH to reach a maximum around 82 % from pH 3.0 onwards. To prevent any metal precipitation, and as most industrial and wastewater is moderately acidic, we decided to work at pH = 5.0 in the subsequent experiments.

**Optimization of mass of resin used**

At pH 5.0, the optimal mass of polymer was determined ( $c_0 \approx 70 \text{ mg L}^{-1}$ ,  $V = 25 \text{ cm}^3$ ). Figure 3 clearly shows that from about 100 mg of polymer onwards, the capture is nearly complete.

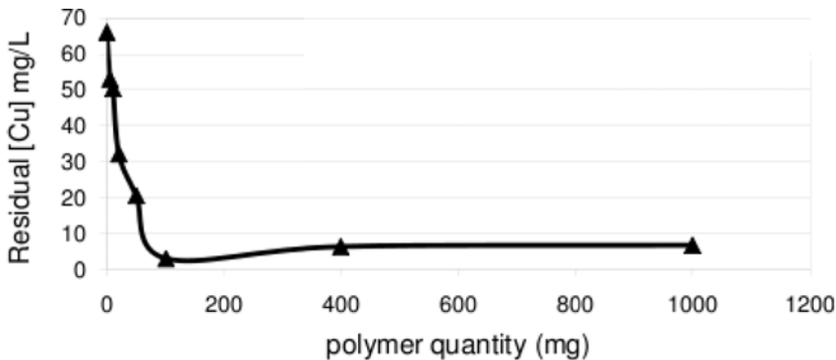


Figure 3 showing the residual copper concentration as the quantity of polymer is increased

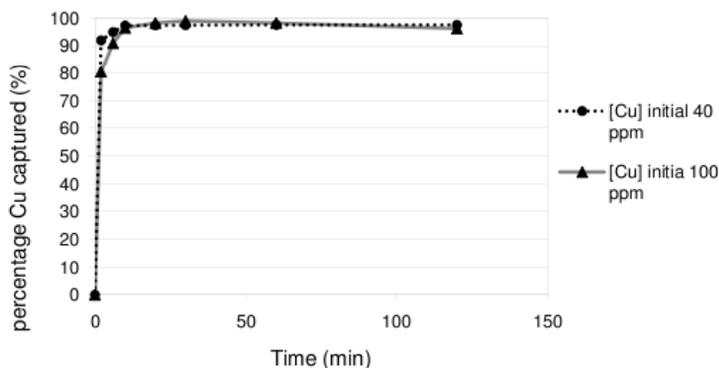


Figure 4 showing the capture of copper against time for a 40 ppm and 100 ppm solution

#### Capture kinetics

The kinetics of capture was studied at 40 ppm and 100 ppm, leading to sorption levels ( $q$ ) of 4.8 and 11.5 mg of copper/g of polymer. As shown in figure 4, Magpie-101 has a very fast kinetics, with more than 95 % capture within the first 10 min of contact. At such a fast sorption rate, it was not possible to model the kinetics.

#### Saturation of the polymer

Saturation of the polymer Magpie-101 by copper can be observed as the concentration of the test solution is increased from 0 to 2500 ppm ( $V = 20 \text{ cm}^3$ , 200 mg of polymer). The contact time for this experiment was kept at 30 min to ensure that the capturing reaction was completed. When plotting the copper concentration against the amount absorbed,  $q$ , one can clearly observe saturation around 120 milligrams of copper per gram of Magpie-101.

#### Effect of calcium on copper sorption

Magpie Polymers do not work based on ionic interactions, but on coordination chemistry. As a result, the polymers are transparent to alkaline or alkaline-earth metals such as sodium, calcium or magnesium. This selectivity is important when aiming to remove toxic or valuable transition metals from water with high ionic strength (Aksu 2007). An experiment was run with 7 different samples containing between 0 and 1000 ppm of calcium and 100 ppm of copper. The solutions, at pH 6.0, were then treated with 200 mg of Magpie-101 for 30 min, and their metal content was determined. Clearly, no adverse effect of the calcium present was found in this experiment as copper capture remained at <95%, irrespective of the calcium concentration.

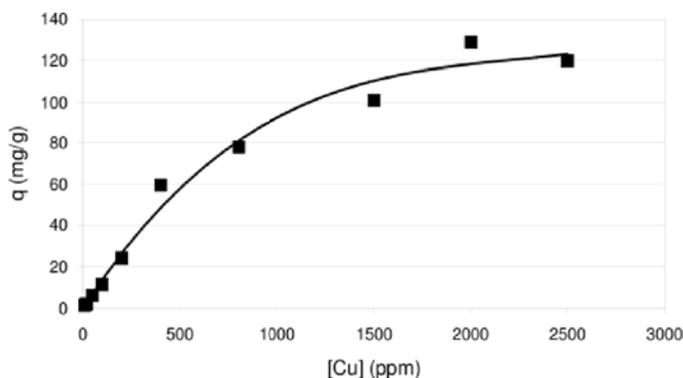


Figure 5 showing the saturation of Magpie-101 with copper ions

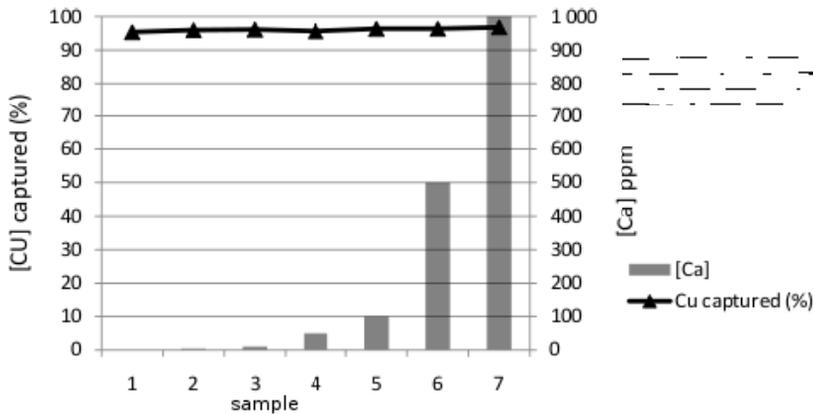


Figure 6 showing copper capture with increasing calcium concentration

### Flow operation of Magpie-101

Rather than operating the polymer in a batch process, a column of the polymer can be prepared. For this experiment, 10 g of polymer was packed into a glass column. With this set-up, a contact time of 1 min was achieved when running a solution at 10 mL/min. The column was run with a Cu(II) containing solution ( $c_0 \approx 30 \text{ mg L}^{-1}$ ,  $V = 1 \text{ L}$ ) and samples were taken every 100 ml. As expected, the capture observed was now higher than 99%, with residual concentration around  $50 \mu\text{g L}^{-1}$  (AAS). We are now investigating the saturation level the polymer can tolerate in this flow set-up.

### Conclusion

From our experimental data, we have learned that Magpie Polymers can be used for the capture of a large number of transition metals. The metals can be recovered and the polymer can be recycled using acid wash. Between the two resins studied, Magpie-101 and Magpie-102, there is a clear selectivity with any given metal. In this paper, the capturing characteristics of Magpie-101 with regards to copper are studied in detail. We observed an optimum pH between 3.0 and 6.0, very fast kinetics compared to more classical ion-exchange based resins (Gaikwad 2009) and a high saturation level. Finally, it was demonstrated that copper sorption for this resin based on coordination chemistry, is not affected by the presence of calcium ions. Current studies now concentrate on the selectivity Magpie Polymers exhibit between different transition metals. Preliminary results show the resins are able to resolve complex mixtures containing two or more transition metals.

### References

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